12 PAINT

12.1 Analytical Approach

12.1.1 The examiner is typically requested to compare a questioned paint sample or questioned paint deposits/smears on an object(s) to known paint samples. Instead of a Q vs K comparison, the examiner may be requested to conduct a make/model determination or to obtain information on an individual paint sample with no known paint sample available.

12.1.2 The examiner first conducts a macroscopic examination of the paint evidence. If appropriate, a fracture match comparison can be conducted. If the evidence to be examined is a liquid paint sample, the liquid is applied to clean glass slides and allowed to dry.

12.1.3 Paint can be characterized by a number of physical and chemical properties. The sample size and type of paint present in the sample will assist the examiner in determining which subsequent tests will be conducted. If the paint sample is an Original Equipment Manufacturer (OEM), includes less than 4 layers or includes a structural paint, the examiner should, if possible, conduct instrumental analysis including fluorescence microscopy, Fourier Transform Infrared Spectrometry (FTIR) with microscope accessory and Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDS) analysis.

12.1.4 During a microscopic examination, the examiner notes any physical properties which assist in characterizing a paint sample. These properties can include color, type (vehicular/ structural; enamel/lacquer; metallic/nonmetallic), texture, thickness, layer sequence and weathering. The microscopic examination is conducted separately for known and questioned paint particles. At this point in the examination, fluorescence microscopy may be useful in assessing the paint.

12.1.5 If sample size permits, the examiner can continue analyzing the paint evidence using side-by-side solubility/microchemical reaction tests and/or instrumental analysis.

12.1.6 For the solubility tests, the examiner observes the solubility of individual paint layers in chloroform, acetone and toluene. Toluene will only be used if a lacquer paint is indicated. For the microchemical reaction tests, the examiner observes the reactions of individual paint layers with certain chemical reagents: LeRosen, Diphenylamine (DPA), concentrated H_2SO_4 and concentrated HNO_3. If a limited amount of questioned paint is present, the examiner will completely characterize the known paint to determine which reagents give the most meaningful results. Those select reagents would then be used side-by-side to compare the Q and K samples.

12.1.7 The examiner can also analyze paint samples using instrumental techniques. FTIR and Pyrolysis Gas Chromatography (PGC) are useful techniques in comparing the organic chemical composition of paint layers. SEM-EDS is useful in determining the elemental chemical composition of paint layers. If sample size and/or condition permits, colorimetry or microspectrophotometry can be conducted on the paint samples for color analysis. If K and Q paints are sufficient for organic and elemental characterization, then fluorescence microscopy will also be employed for comparison of the samples.

12.1.8 After the analytical data has been obtained, the examiner compares the data for the known and questioned paint samples to evaluate the possible association of the K & Q.

12.1.9 For a make/model determination, the examiner analyzes the questioned sample to determine if an OEM sequence is present. If an OEM sequence is present, each layer of the paint will be analyzed via FTIR. Appropriate information for each layer is entered into the currently available reference collection of known automotive paints, the Paint Data Query (PDQ) database, and a search is conducted. If successful, the search results will be reported as to the possible make, model and range of years in which the OEM sequence may have been used. If no OEM or a partial OEM sequence is present, report the topcoat color of the paint and whether the paint is metallic or nonmetallic.

12.1.9.1 If assistance from the Royal Canadian Mounted Police (RCMP) PDQ Maintenance Team is needed, contact the Central Trace PDQ resource person or the Section Chief.

12.2 Paint Recovery Techniques

12.2.1 Purpose

To recover foreign paint that might be present on an item of evidence to allow analysis of paint samples.

12.2.2 Minimum Standards and Controls

12.2.2.1 The examiner must change the examination paper between victim and suspect or scene exhibits.

12.2.2.2 The examiner may change the paper between multiple victim, suspect or scene items, as necessary.

12.2.2.3 The examiner must change gloves and clean their tools between examining the evidence from the victim and the evidence from the suspect.

12.2.3 Analytical Procedures

12.2.3.1 Thoroughly clean the examination area prior to the evidence being retrieved.

12.2.3.2 Remove the item of evidence from the container and place it upon a clean sheet of paper. Note and record the condition of the evidence.

12.2.3.3 Conduct a thorough inspection of the item for any visible paint particles/deposits. These are collected in evidence containers which may include plastic or metal boxes, glassine envelopes, weighing paper or a paper evidence fold.

12.2.3.4 If no paint particles/deposits are readily observed, the examiner will use a magnifier/viewer or stereomicroscope for searching purposes. If tears or other damage are observed on an item, these areas may be cut out for further analysis. If particles/deposits are not observed and the evidence consists of clothing articles then scraping will be conducted.

12.2.3.5 Scraping is done by holding or suspending the item over a clean sheet of paper and scraping the evidence thoroughly using a clean spatula. Any recovered debris is collected in an evidence container for further analysis.

12.2.3.6 The evidence must be sketched or otherwise documented to note the locations of any probative tears, paint deposits/smears or other unusual features. If only damage from medical rescue personnel is present, no sketching or documentation other than written notes is performed.

12.2.4 References

12.2.4.1 Thornton, John I., “Forensic Paint Examination”, Forensic Science Handbook, Volume 1, Second Edition, Pearson Education, Inc., 2002, pp. 429-478.

12.3 Macroscopic/Microscopic Examination

12.3.1 Purpose

To examine submitted paint evidence on a macroscopic and microscopic scale, noting physical properties, generally as the first step in the characterization and comparison of known and questioned paint samples.

12.3.2 Minimum Standards and Controls

12.3.2.1 Clean tools and work areas are a must.

12.3.3 Analytical Procedures

12.3.3.1 Thoroughly clean the examination area prior to the evidence being retrieved.

12.3.3.2 The sample is examined with a stereomicroscope and the physical properties of each paint sample are noted and recorded on a worksheet (Appendix 19). Document the approximate color and thickness of each layer by coloring the wedge on the worksheet. The layer sequence, color, type, texture, thickness and any unusual features are noted for each sample. The examiner can also use the comparison microscope or the polarized light microscope in determining the physical characteristics of a paint sample.

12.3.3.3 Paint particles may be manipulated with fine forceps and may be dissected using a fine scalpel blade to allow the examiner to thoroughly characterize the physical properties.

12.3.3.4 Mineral oil or water should be used to compare the K & Q paint particles side-by-side on black and white backgrounds with varying intensities of light.

12.3.3.5 If any significant differences are observed between the questioned and known particles, such as color, the examiner can discontinue the analysis.

12.3.4 References

12.3.4.1 "The Evidential Value of Automobile Paint Chips", Ryland, S.G. and Kopec, R.J., *Journal of Forensic Sciences*, Vol 24(1), 1979, pp. 140-147.

12.3.4.2 "Evaluation of Automobile Paint Flakes as Evidence", Gothard, J.A., *Journal of Forensic Sciences*, Vol 21(3), 1976, pp. 636-641.

12.4 Microchemical Tests

12.4.1 Purpose

To determine the solubility and chemical reactivity of individual paint layers in known and questioned samples.

12.4.2 Safety Considerations

12.4.2.1 Concentrated acids and solvents should be used in a well-ventilated area with proper precautions being exercised to minimize skin contact.

12.4.3 Minimum Standards and Controls

12.4.3.1 Solvents and chemical reagents are prepared as prescribed in Appendix 4.

12.4.3.2 Appendix 4 also contains the prescribed materials to check the reagents to ensure they are working properly.

12.4.3.3 The following chemicals should be reagent grade or better:

acetone, chloroform, diphenylamine, concentrated sulfuric acid, concentrated nitric acid, formaldehyde, glacial acetic acid, and toluene

12.4.4 Analytical Procedures

12.4.4.1 The examiner will conduct each test on both the known and questioned paint particles in a side-by-side comparison.

12.4.4.2 Place paint particles in a welled (or depression) slide, a spot plate or on a microscope slide in the field of view of a stereomicroscope.

12.4.4.3 Apply the reagent or solvent directly to the particles. Any resulting reaction, or lack thereof, is noted on the paint worksheet. The effect of each reagent on the individual paint layers of the questioned particle is compared to that of the corresponding layers of the known particle.

12.4.4.4 Sample size and type will assist the examiner in determining which tests will be conducted.

12.4.4.5 If a sufficient quantity of paint is available the following will be used as a minimum: chloroform, acetone, (toluene, if appropriate), diphenylamine, LeRosen, concentrated HNO_3 and concentrated H_2SO_4.

12.4.4.6 If any significant differences are observed between the questioned and known particles, the examiner can discontinue the analysis.

12.4.5 References

12.4.5.1 "Application of the LeRosen Test to Paint Analysis", Linde, H.G. and Stone, R.P., *Journal of Forensic Sciences*, Vol 24(3), 1979, pp. 650-655.

12.4.5.2 "Solubility Characterization of Automotive Paints", Thornton, J.I., Kraus, S., Lerner, B. and Kahane, D., *Journal of Forensic Sciences*, Vol 28(4), 1983, pp. 1004-1007.

12.5 Fluorescence

12.5.1 Purpose

To determine and compare the fluorescence characteristics of paint samples, deposits or smears.

12.5.2 Safety Considerations

12.5.2.1 Do not look directly into the fluorescence source.

12.5.3 Analytical Procedure

12.5.3.1 Paint samples, deposits or smears are subjected to different ranges of wavelengths and the resulting fluorescence colors or lack thereof are noted on the fluorescence worksheet.

12.5.3.2 Paint samples, deposits or smears may be examined "dry" or mounted in a suitable "non-fluorescent" mounting medium, however, questioned and known samples should be examined simultaneously; side-by-side using the polarized light microscope.

12.5.3.3 Fluorescence cubes to be used are **WU** (wide UV 330 – 385 nm), **WBV** (wide blue violet – range 400 – 440 nm), **WB** (wide blue – range 450 – 480 nm) and **WG** (wide green – range 510 – 550 nm). These filter blocks include excitation and barrier filters.

12.5.3.4 Paint smears are usually not homogeneous. Great care should be employed when interpreting the results of the comparison of paint smears with paint particles; some variation in fluorescence properties is expected. In addition, when two paint samples are compared, small differences may be seen if one of

the samples has been subjected to sunlight more often than the other sample e.g., paint from a vehicle's hood compared to paint from the bottom portion of a fender.

12.5.3.5 Caution should be taken when eliminating samples based upon fluorescence data alone. Detailed notes explaining the basis for the elimination are a must. Eliminations based upon fluorescence will be reported as "due to differences in chemical composition".

12.6 Instrumental Analysis

12.6.1 FT-IR

12.6.1.1 Safety Considerations

12.6.1.1.1 Do not look directly into the laser source.

12.6.1.1.2 The MCT detector for the microscope accessory must be cooled with liquid nitrogen. Insulated gloves and safety glasses shall be worn when filling the transport dewar as well as the instrument reservoir.

12.6.1.2 Minimum Standards and Controls

12.6.1.2.1 Ensure that the daily QC has been performed (Refer to Appendix 6).

12.6.1.2.2 Replicate analyses may be employed to ensure reproducibility or to demonstrate variability within a sample.

12.6.1.3 Analytical Procedures

For the examination of the individual layers of paint in a particle, the examiner must prepare the particle for analysis.

12.6.1.3.1 The sample may be prepared by using a scalpel to remove a very thin cross-section of any/all paint layers. This is followed by further sample flattening using a roller or microcompression cell with diamond windows.

12.6.1.3.2 Alternatively, a very low angle cut may be made to expose the paint layers and each layer may be sampled one at a time for use in the microcompression cell.

12.6.1.3.3 The flattened sample is placed on a KBr window or left in the microcompression cell. With the FTIR microscope accessory, the examiner adjusts the aperture edges to mask all but individual layers. Spectra are obtained for each layer, when possible, using standard methods which are printed and stored with the instrument.

12.6.1.3.4 Generally speaking, data manipulation, including baseline correction, is discouraged and smoothing of data is prohibited. If baseline correction is conducted, a copy of the original, uncorrected spectrum will be included in the case file.

12.6.1.3.5 The spectra for the known and questioned layers are compared. The resolution of standard reference spectra will be equal to or better than the resolution of the sample spectra.

12.6.1.3.6 If any significant differences are observed in the spectra of the questioned and known sample, the examiner can discontinue the analysis.

12.6.1.4 References

12.6.1.4.1 "FT-Infrared Spectroscopy of Automobile Paints using Infrared Microscopy", Stoecklein, W. and Gloger, M., *Nicolet FT- IR Spectral Lines*, Spring- Summer 1988, pp. 2-6.

12.6.1.4.2 "Forensic Applications of IR Microscopy", Compton, S. and Powell, J., *American Laboratory*, Nov 1991, pp. 41- 51.

12.6.2 Pyrolysis Gas Chromatography (PGC)

12.6.2.1 Safety Considerations

12.6.2.1.1 The pyroprobe coil is heated to extremely high temperatures (1200 ^{o}C) and great care should be taken in handling.

12.6.2.2 Minimum Standards and Controls

12.6.2.2.1 The QC using the polyethylene standard film must be run prior to case samples. (Refer to Appendix 7)

12.6.2.2.2 Replicate analyses may be employed to ensure reproducibility or to demonstrate variability within a sample.

12.6.2.3 Analytical Procedures

12.6.2.3.1 Refer to the GC conditions sheet for pyrolysis settings. The pyroprobe unit setting is determined by the reading obtained during the QC. (Refer to Appendix 7.J.).

12.6.2.3.2 Prepare the samples for pyrolysis GC analysis by cutting a small piece from the questioned and known samples. These samples should be approximately the same size and include all layers.

12.6.2.3.3 A clean quartz tube is placed in the pyroprobe coil and a blank run is conducted to ensure that the quartz tube is blank. Following this initial run, the known and questioned samples are analyzed with a blank run inserted between each sample. Following each run, the quartz tube is cleaned thoroughly by baking at 1200^{o}C for 5 seconds.

12.6.2.3.4 The pyrograms for the samples are printed and are compared by overlaying them one on the other.

12.6.2.3.5 If any significant differences are observed in the pyrograms of the questioned and known samples, the examiner can discontinue the analysis.

12.6.2.4 References

12.6.2.4.1 "The Analysis of Automotive Paints by Pyrolysis Gas Chromatography", Levy. E.J., *Analytical Pyrolysis*, 1977, pp. 319- 335.

12.6.2.4.2 "Pyrolysis-Gas Chromatographic Examination of Paints", Cardosi, P.J., *Journal of Forensic Science*, Vol 27(3), 1982, pp. 695- 707.

12.6.3 Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDS)

12.6.3.1 Safety Considerations

12.6.3.1.1 The EDS detector system must be cooled with liquid nitrogen. Insulated gloves and safety glasses shall be worn when filling the dewar.

12.6.3.1.2 Be aware of elevated temperatures when changing a filament which has been in operation.

12.6.3.2 Carbon Evaporation

Refer to Gunshot Residue Analysis, ¶ 10.2.

12.6.3.3 Minimum Standards and Controls

12.6.3.3.1 To minimize take-off angle effects, paint samples should be flat and mounted normal to the electron beam.

12.6.3.4 Analytical Procedures

12.6.3.4.1 A sample stub is prepared by affixing either a carbon disk or a carbon adhesive tape disk to the aluminum stub.

12.6.3.4.2 The sample is mounted on the carbon adhesive tape (flat for single layer paint or on edge for multilayered paint, shavings may also be used) or on the carbon disk (use starch glue). Due to potential heterogeneity within the paint layer, the sample should be at least 2mm in length whenever possible.

12.6.3.4.3 Carbon glue is applied to edges of paint particle to ensure that the sample makes adequate electrical contact with the sample stub.

12.6.3.4.4 The sample is carbon coated.

12.6.3.4.5 The sample stub is mounted in an SEM vacuum chamber which is then pumped down to the standard vacuum for analysis.

12.6.3.4.6 The filament is turned on and saturated at 20kV, and a gain calibration is performed on the EDS detector.

12.6.3.4.7 An X-ray spectrum is collected from each layer of each sample (K and Q). The spectrum should be a composite of at least 4 separate areas on each layer of paint. A hard copy is printed to document the elemental composition. Spectral files are stored in electronic form and archived.

12.6.3.4.8 Comparison of K and Q samples is made on a qualitative basis; some variation in elemental concentration is allowable.

12.6.3.4.9 Results are included with the Instrument Support Request form.

12.6.3.5 References

12.6.3.5.1 “Analysis Protocol for Discrimination of Automotive Paints by SEM- EDXA Using Beam Alignment by Current Centering”, Beam, T.L. and Willis, W.V., *Journal of Forensic Science*, Vol 35(5), 1990, pp. 1055- 1063.

12.6.4 Colorimetry

If known and questioned paint particles are generally flat and in good condition and are a minimum of 4 mm in diameter, then they must be referred for comparison of the top coat colors. Generally speaking, colorimetry will only be conducted on suitable samples that require all instrumental testing.

12.6.5 Microspectrophotometry

12.6.5.1 The microspectrophotometer (MSP) may be useful for the comparison of the colors of known and questioned paints. The samples must be mounted perpendicular to the axis of the microscope and the upper surface of the clean paint must be in focus. While location information is not always readily available, the known paint samples should originate as close as possible to the questioned paint sample. Additionally, obtaining the same data from a K and Q paint does not mean that the pigments are the same rather only that the colors are not distinguishable by the MSP.

12.6.5.2 The examiner must be aware of and familiar with these and other variations that can occur when interpreting the data obtained from the comparison of paints.

12.6.5.3 The DFS instruments are equipped with 15X reflecting objectives (also known as Cassegrain objectives) and different brightfield objectives. Brightfield objectives are not suitable for microspectrophotometry in reflectance mode. Although the reflecting objectives are manufactured specifically for reflectance mode microspectrophotometry, the results obtained when using these objectives are poor. In order to get good spectral data in reflectance mode, either darkfield or 45^{o} oblique objectives are required.

12.6.5.4 At present, spectral data for paint can only be obtained by transmittance mode microspectrophotometry of thin sections. In order to obtain reliable data comparing K and Q paints, thin sections should have consistent thickness.

12.6.5.5 Given the above discussion, microspectrophotometry may be used for paints but it is not one of the required instruments for paint comparisons.

12.6.5.6 References

12.6.5.6.1 Stoecklein, Wilfried, “The role of colour and microscopic techniques for the characterisation of paint fragments”, Forensic Examination of Glass and Paint: Analysis and Interpretation, Taylor and Francis, 2001, pp.156-161.

12.7 Documentation

12.7.1 As a minimum, each case file will include a paint worksheet(s) (as applicable), any notes detailing physical properties and item description, hard copies of all spectra or pyrograms generated during the analysis and conditions sheets for all instrumental analyses conducted.

12.7.2 FTIR spectra will be printed as follows:

- Split at 2000 cm^{-1}
- X-axis limits, with the microscope accessory, 4000 cm^{-1} to 650 cm^{-1}
- The spectrum will take up the maximum amount of space on the page as is possible
- One spectrum per page

12.7.3 FTIR spectra will be labeled as follows:

- FS Lab #, Item # and how prepared (e.g., diamond cell)
- Date and time
- Filename (optional)

12.7.4 Generally speaking, in addition to color, texture, type and layer sequence (if applicable) one, two or three layer paint particles require organic and elemental composition comparison. Four layer original finish automotive paints would also require organic and elemental composition comparison. Four and five layer paints require organic and elemental composition comparison at the examiner's discretion. Six layers and greater of automotive paint does not require composition comparison. Six layers and greater of structural paint require composition comparison at the examiner's discretion.

12.8 Report Wording

12.8.1 For paint cases where multilayered particles with matching K and Q samples:

The multilayered paint particles in Items 1 and 2 matched in colors, textures, types and layer sequence.

12.8.2 For paint cases where multilayered paint particles with feathering effects or missing layer structure, but with everything else matching:

The multilayered paint particles in Items 1 and 2 matched in corresponding (or respective) colors, textures, types and layer sequence.

12.8.3 For paint particles requiring FTIR and/or PGC, SEM/EDS under the method protocol add:

"... and chemical composition."

12.8.3.1 "Chemical composition" includes both organic and elemental composition. There may be an occasion when one or both of these terms is used in lieu of "chemical" composition.

"organic composition, elemental composition"

12.8.4 The use of the term "matched" must be accompanied by what the particles "matched" in (colors, textures, types and so on). This term is generally used when there are no unexplainable differences in the testing conducted on the known and questioned samples. It is recognized that there may be instances when, based upon the data, the term "consistent" or the term "similar" may be more appropriately substituted for "matched".

12.8.4.1 There may be an occasion when these terms are used in the same sentence:

The multilayered paint particles in Items 1 and 2 matched in colors, textures types and layer sequence and were consistent in chemical composition.

12.8.5 If the particles are different:

12.8.5.1 The paint particles in Items 1 and 2 could not be associated due to differences in color. (or any of the following criteria: type, texture, layer sequence, chemical composition)

12.8.5.2 Green paint smears present on Item 1 could not be associated with the Item 2 green paint due to differences in chemical composition.

12.8.6 If sample size or condition precludes a full examination:

The paint particles in Items 1 and 2 matched in colors and types and could have .... OR in whatever tests you did. (Depending upon the evidence present, it may be appropriate to also add the statement…"Sample condition precluded a complete analysis.".)

12.8.7 The sample condition (which includes sample amount) precluded a complete analysis and no conclusion could be drawn from what data does exist:

12.8.7.1 The condition of the Item 1 smears precluded a complete analysis for comparison with the Item 2 paint.

12.8.7.2 No meaningful comparison could be made with Item 1 due to the sample condition of Item 2.

12.8.8 If no paint was recovered:

No paint was recovered from Item 1 for comparison to Item 2.

12.8.9 Color should be used and number may be used in any of the above examples to indicate number of particles and color of particles examined (e.g., "One multilayered red nonmetallic paint particle...")

12.8.10 After the examiner has used one of the paint statements, a conclusion usually follows and ends the reporting results prior to describing the disposition of the evidence on the Certificate of Analysis. These conclusions appear in order of "strength":

12.8.10.1 It was concluded that the paint in Items A-Z could have had a common origin.

12.8.10.2 It was concluded that the Item ___ paint could have had a common origin with Item ___.

12.8.10.3 The smears on Item ___ and the Item ___ paint could have had a common origin.

12.8.10.4 It was concluded that the paints in Items A-Z either originated from the same source or different sources painted in the same manner.

12.8.10.5 It is considered unlikely that the paint in Item ___ originated from any source other than the _____ vehicle OR originated from any source other than the _____ vehicle represented by Item ___.

12.8.10.6 It is considered remote that the interchange of paints described above occurred in any manner other than the contact of the two vehicles (or objects).

12.8.10.7 It is considered extremely remote that the interchange of paints described above occurred in any manner other than the contact of the two vehicles (or objects).

12.8.11 For samples where a search of the PDQ, paint database was successful:

12.8.11.1 A search of the PDQ (Paint Data Query) database indicates that the Item __ foreign paint was consistent with paint used on the following vehicles: [List them. E.g., 1998-1999 Toyota Camry and Toyota Avalon] It should be noted that all makes/models/years are not represented in the database.

12.8.12 For samples where an OEM sequence is not present:

12.8.12.1 The red metallic paint (paint particles, paint smears) present (in the debris from, on) Item __ was consistent with (indicative of) a repaint; therefore, no make/model determination could be made.

12.8.12.2 Item 1 consisted of a foreign black nonmetallic paint particle that was not suitable for make/model determination.

12.8.13 For recovered paint where knowns are being requested for comparison purposes the report will generally read:

Foreign (color and metallic or nonmetallic) paint was recovered from Item __ which was suitable for comparison purposes. If a known source of paint is located, resubmit Item __ along with the known paint for comparison.

♦End